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We have performed quantitative high-resolution transmission electron microscopy studies of the structure of shear bands in metallic glasses. We observe the formation of numerous nanometer-scale voids in shear bands produced under predominantly tensile loading. These void-like defects appear to result from the coalescence of excess free volume in the active shear band when the plastic flow ceases. By comparing the free energy of the shear band with that of the undeformed glass, we show that the void formation process is thermodynamically possible. The presence of the voids can explain several features of the mechanical behavior of metallic glasses, including the difference in plastic strain observed between tests conducted in uniaxial tension and those done in uniaxial compression.

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Foreword

Bulk metallic glasses have unique mechanical and physical properties (including high strength, large elastic limits, and a distinct glass transition) that make them attractive candidates for engineering applications. The non-crystalline structure of these amorphous alloys means that their mechanical behavior is qualitatively different from that of conventional crystalline alloys. In particular, at low temperatures metallic glasses deform by localization of shear into very narrow shear bands. This makes metallic glasses potentially attractive materials to replace depleted uranium in kinetic-energy armor-penetrating projectiles. Development of metallic glasses for these kinds of applications, however, requires an understanding of fundamental aspects of their mechanical behavior.

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1 Problem Statement

This research project was focused on providing detailed observations of the structure and behavior of shear bands in metallic glasses, with the goal of enhancing our understanding of inhomogeneous deformation more generally. The specific objectives, as stated in the original proposal, were:

1. Identify the atomic-scale structural changes accompanying plastic deformation, and from this deduce the mechanism(s) of shear band nucleation in metallic glasses;

2. Characterize the interactions of shear bands with second-phase particles and fibers, with particular attention to the effect of reinforcements on shear band nucleation and motion. As part of this effort, we will design, produce, and evaluate new metallic-glass-matrix composite materials.

As the project progressed, it became apparent that the first objective was a significant challenge in its own right, and most of our efforts were devoted to it (as described below). The results obtained represent a significant contribution to the understanding of inhomogeneous deformation in metallic glasses, and laid the groundwork for our continuing efforts in this area (funded now by the National Science Foundation). Due to our focus on the first objective, we made only limited progress on the second, focusing mostly on the effect of medium-range order on shear band propagation. However, we did also make the first observations to correlate shear band behavior directly with stress-strain curves (*in situ* during loading), which shed some light on shear band initiation and motion in monolithic metallic glasses.

2 Research Results

2.1 Structure of shear bands in metallic glasses

The central idea behind the original proposal was that some significant insight into the mechanisms of inhomogeneous deformation of metallic glasses might be gained by detailed observations of the structure of the shear bands themselves. Such observations, however, represent a significant challenge, for two reasons. First, shear bands in metallic glasses are very thin ($\sim$10-20 nm) and usually represent only a small volume fraction of the material. This means that bulk structural characterization techniques (such as x-ray or neutron scattering) are of limited utility, as they average over a much larger volume of material. This means that electron-based techniques, and transmission electron microscopy (TEM) in particular, must be employed. This choice leads to the second challenge, which is in finding a mechanism by which to observe the shear bands. Most of the contrast mechanisms used for TEM examination of conventional metals rely on the fact that these materials are crystalline and thus cause strong Bragg scattering of the electrons; observation of defects (such as dislocations and grain boundaries) is possible because they locally disrupt this Bragg scattering. In an amorphous material, on the other hand, there is only relatively weak diffuse scattering by the amorphous structure, making it impossible to observe defects in this way.

In the original proposal, we contemplated using extended energy-loss fine structure (EXELFS) spectroscopy to study the atomic-scale structure of the deformed material inside shear bands in metallic glasses. We made some preliminary observations of Zr-based bulk metallic glasses using this technique, with limited success. The primary problem is that the signal-to-noise ratio of EXELFS is limited, particularly for the relatively high atomic number elements involved. (High atomic number elements have energy loss peaks at high energies, where the EXELFS signal is quite weak.) Because the technique described below turned out to work quite well, we did not pursue the EXELFS technique beyond these initial trials. We do believe, however, that EXELFS still has significant potential for examining metallic glasses, particularly those based on low-Z elements (such as Al and Mg) which have their loss peaks at lower electron energies.

2.1.1 Identification of defects in shear bands

To examine the structure of shear bands in metallic glasses, we adapted a TEM technique initially developed by Miller and Gibson for identifying nanometer-scale voids in amorphous silicon dioxide [1]. This technique, which is described in more detail in one of our publications [2], involves the following steps:

1. A high-resolution transmission electron microscope (HRTEM) image is collected from an area of the sample that contains both deformed (shear band) and undeformed regions (Figure 1). It is important that the specimen be thin (∼5-10 nm), so that the weak-phase-object approximation applies (which is used in the subsequent analysis). In such an image, the contrast arises from the projected potential that an electron sees in transiting the specimen–regions of high projected potential appear dark, while regions of low projected potential appear bright [3].

2. Two regions of the image are selected, one from the shear band and one from undeformed material, are selected and Fourier-transformed to reciprocal space. The two-dimensional Fourier transforms are then azimuthally averaged to yield one-dimensional equivalents (Figure 2). In these 1D transforms, we always observe a peak at a spatial frequency of $k \sim 1$ nm^{-1}. This peak is always more prominent in the deformed material, and is also observable using conventional dark-field TEM techniques [4, 5]. This suggests that there are nanometer-scale features present in the structure of the glass, that are more numerous in the shear band than in the undeformed region.

3. To image these structural features, we apply an annual filter to the 2D Fourier transform, and perform an inverse Fourier transformation back to real space (Figure 3(a)). Notice that the length scale of the features in this image is ∼1 nm. Most of the features are due to statistical fluctuations in the projected potential, but some are larger fluctuations due to the presence of defects.

4. To determine which features are statistical and which represent true defects, we plot a histogram of the brightness of the filtered image (not shown), and determine the standard deviation σ of the brightness distribution. We then apply a threshold filter which only passes regions of the filtered image that exceed the mean brightness by at least 3σ (Figure 3(b); note that the contrast has been reversed for better reproduction).

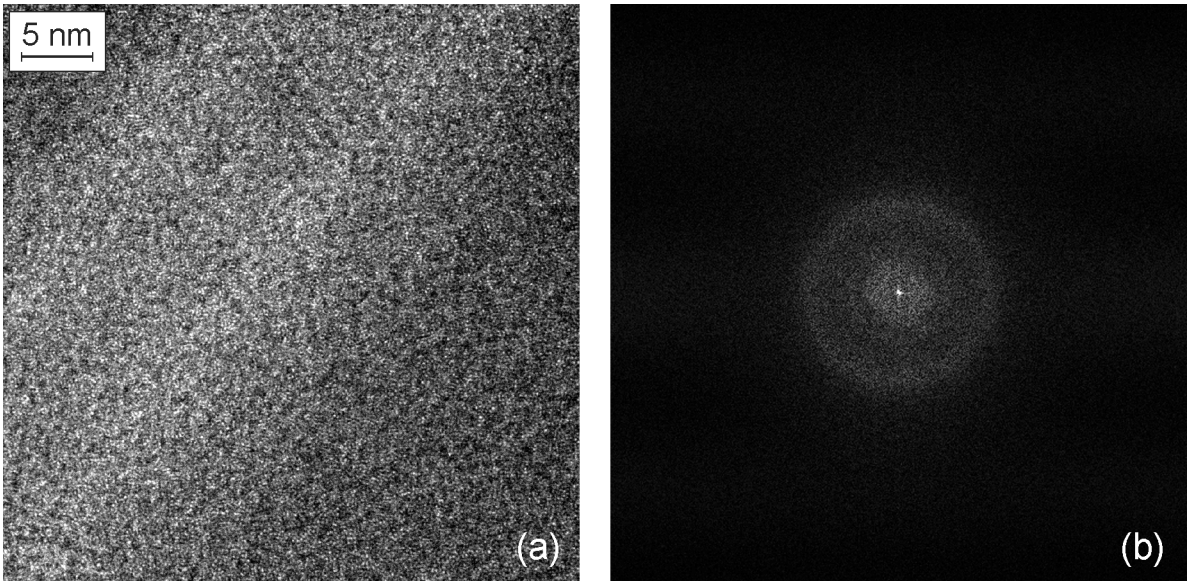

Figure 1: (a) HRTEM image of a shear band formed ahead of a crack tip in a $Zr_{57}Ti_5Cu_{20}Ni_8Al_{10}$ metallic glass. The contrast in the shear band region is lighter than the undeformed material, because the shear band region is somewhat thinner. (b) Two-dimensional Fourier transform from the shear band region; note the amorphous 'halo' and the relatively strong scattering near the central spot.

The structural features in Fig. 3(b) are regions of statistically low projected potential; since the projected potential is related to the atomic density, we believe that the most likely explanation is that they represent nanometer-scale voids present inside the shear bands.*

The existence of such voids in shear bands was inferred by Donovan and Stobbs, on the basis of electron scattering data [5]. They speculated that if an applied shear stress created excess free volume in a shear band, then when the shear stress was removed the excess free volume would coalesce into small voids. Quantitative high resolution electron microscopy, as described here, allows us to image these voids directly, and obtain quantitative information about their size, numbers, and distribution. Using this information, we can begin to understand the formation and behavior of defects. For instance, let us assume that all of the void volume was uniformly distributed as free volume in the active shear band. Based on the size and number density of the voids, we can estimate that the active shear band had approximately 0.4% more volume per atom than the undeformed material. This is comparable to the change in volume associated with structural relaxation of a metallic glass due to annealing [6].

2.1.2 Thermodynamics of void formation

We can also demonstrate that the formation of the voids is a thermodynamically favorable process. For the isothermal formation of the voids by coalescence of free volume to be thermodynamically possible, the free energy of the disordered material of high free volume

*The size of the features in Fig. 3(b) is deceptively small; a more accurate notion of the size can be inferred from the filtered image, Fig. 3(a).

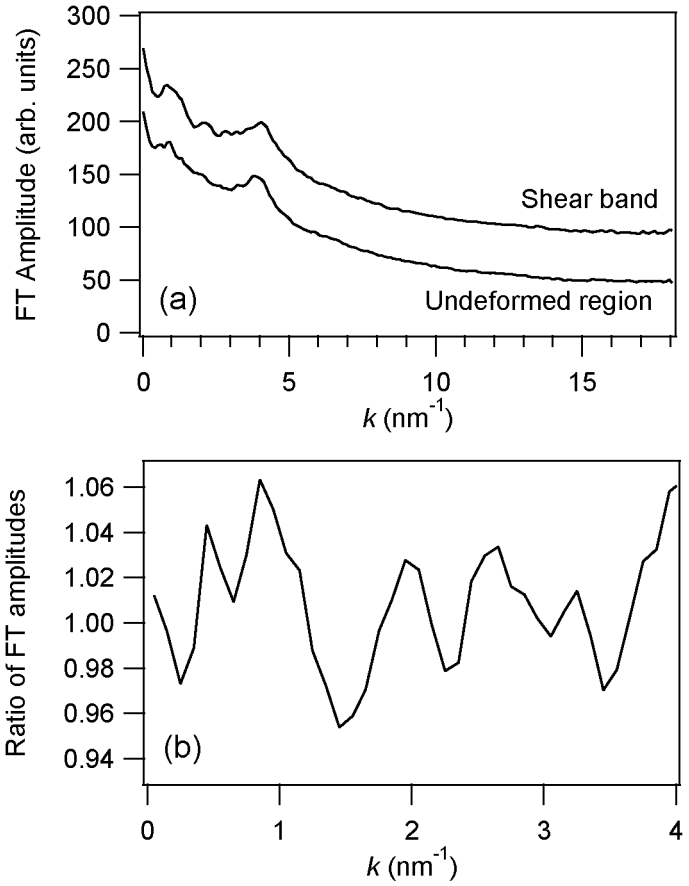

Figure 2: (a) Azimuthially-averaged one-dimensional Fourier transforms calculated from the two-dimensional Fourier transforms of HRTEM images from the shear band and undeformed material. The amorphous 'halo' shows up as a peak near $k = 4.1$ nm^{-1}. Notice the peak near $k = 1$ nm^{-1}, which is stronger for the shear band region than the undeformed material.. (b) Ratio of the two traces from (a), showing the peak near $k = 1$ nm^{-1}. Although barely discernible against the noise, we have observed similar features from images several samples, leading us to conclude that it is a real effect.

in the shear band ($G_{\rm sb}$) must be greater than that of the relaxed material ($G_{\rm glass}$) plus the free energy associated with the voids ($G_{\rm voids}$). The latter arises primarily from the surface energy. For the observed size (1 nm) and concentration (one per 100 nm^3) of the voids, a typical surface energy of 1 J/m^2 gives $G_{\rm voids}$=360 J/mol.

We estimate $G_{\rm sb}$ by considering that the shear-disordered, low-viscosity glass with excess free volume has a fictive temperature $T_{\rm f}$ greater than the glass transition temperature $T_{\rm g}$ of the bulk material. That is, we assume that the structure of the glass with excess free volume at low temperatures is similar to that of the undercooled liquid above $T_{\rm g}$. Figure 4 illustrates the temperature dependence of the difference in equilibrium free energy between the undercooled liquid and the crystal ΔG as calculated from measurements of the entropy of fusion and the difference in the specific heats. When, upon cooling, the liquid becomes configurationally frozen at a temperature $T_{\rm f}$, its configurational entropy ΔS (the difference

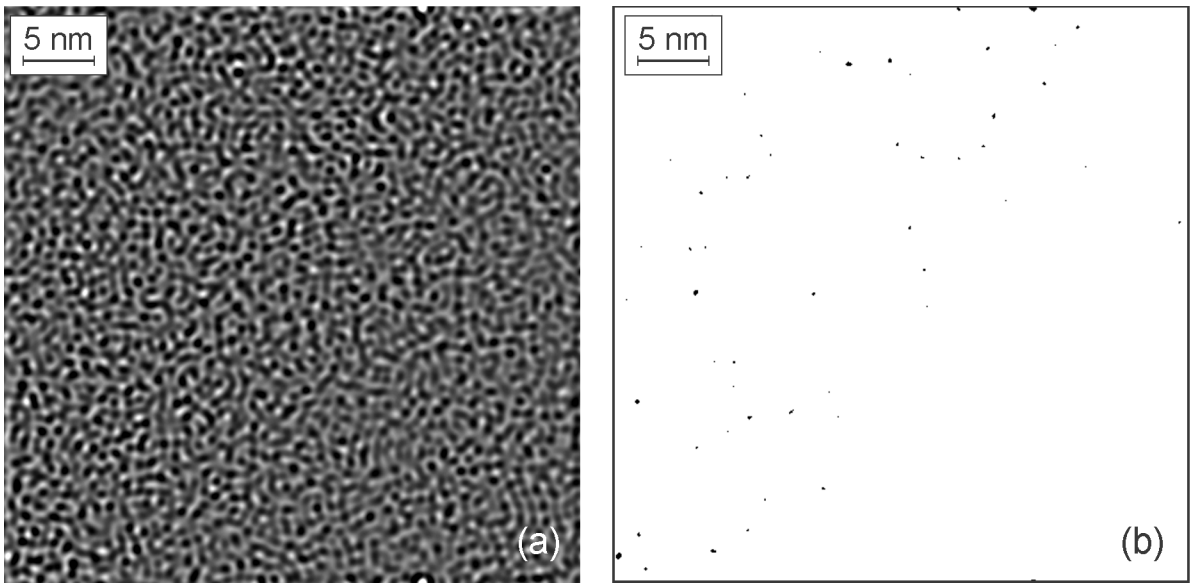

Figure 3: (a) Fourier-filtered real space image, calculated using an annular filter to emphasize structural features with a spatial frequency of $k \sim 1$ nm^{-1} (the peak identified in Fig. 2). (b) The image from (a), with a threshold filter applied to reveal features with an intensity more than 3σ above the average intensity. (The contrast has been inverted for better reproduction.) Notice that the features identified in this way are concentrated in the shear band.

between its entropy and that of the crystal) at lower temperatures remains constant at $-(d\Delta G/dT)_{T_\mathrm{f}}$, and ΔG increases linearly with further decreases in temperature. For the bulk material, T_f=T_g, and its free energy difference below that temperature is $\Delta G_\mathrm{glass}(T)$. The material in the disordered shear band has a fictive temperature $T_\mathrm{f} > T_\mathrm{g}$, and its free energy difference is $\Delta G_\mathrm{sb}(T)$. The isothermal difference in free energy between the two states due to the excess free volume, $\Delta G_\mathrm{fv} = G_\mathrm{sb} - G_\mathrm{glass} = \Delta G_\mathrm{fv} - \Delta G_\mathrm{glass}$, must be greater than G_voids.

$\Delta G(T)$ has been determined experimentally for another Zr-based bulk metallic glass, $Zr_{52.5}Ti_5Cu_{17.9}Ni_{14.6}Al_{10}$ [7]; the results are shown in Fig. 4. The glass transition temperature is $T_\mathrm{g} = 685$ K. The excess free energy due to the excess free volume in the shear band, ΔG_fv, is large enough to provide the free energy to form the voids ($G_\mathrm{voids} = 360$ J/mol) if $T_\mathrm{f} = T_\mathrm{g} + 33$ K. This value of T_f is physically eminently plausible. Since the viscosity is a strong function of fictive temperature, its value at $T_\mathrm{g} + 33$ K is several orders of magnitude lower than that at the glass transition temperature.[†] The volume of the voids corresponds to about 0.4% of the total, a value similar to the typical density increases observed during structural relaxation of glasses below T_g [6], which also lead to large viscosity increases [8].

So far, we have only established that the formation of the voids from a disordered shear band is thermodynamically possible. The kinetics of this 'cavitation' process, however, remain unexplored. It remains to be explained, for example, why the extra free volume

[†]Note that we do not appeal to adiabatic heating for the lowering of the viscosity; the effect is exclusively a structural one. Adiabatic heating, if it occurs, must be preceded by shear localization. Furthermore, in most metallic glasses the thermal conductivity is too high and the shear bands too thin for substantial adiabatic heating to occur.

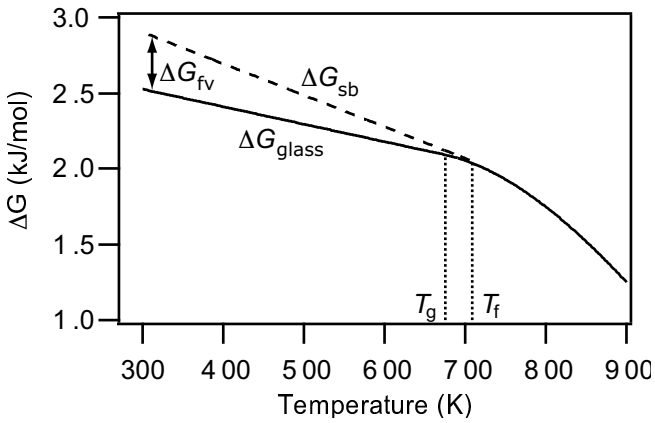

Figure 4: Free energy as a function of temperature for an undeformed Zr-based metallic glass (solid line), and for a deformed region modeled as having structure similar to that of a glass above its glass transition temperature (dashed line).

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in the shear band becomes concentrated in voids, whereas during annealing it is removed elastically from the sample and no voids are formed. A mechanism that combines the nucleation kinetics of the voids and hydrodynamic effects in the surroundings is needed for further progress. Recently, we (in collaboration with Wright and Nix from Stanford) have developed a more sophisticated model for void nucleation, which allows us to calculate the critical void size [9]. This is on the order of 1 Å, which suggests a very large driving force for void nucleation.

2.1.3 Implications for understanding mechanical behavior

The observation of nanometer-scale voids in shear bands has several implications for our understanding fundamental aspects of inhomogeneous deformation in metallic glasses. It provides reasonably direct evidence that dilatation occurs in shear bands, which would support the free volume theory of shear localization. Other evidence, including positron annihilation measurements [10] and observations of relatively small temperature increases in shear bands [11] also indicate that the decreased viscosity of a shear band is due to an increase in free volume, and not to adiabatic effects.

The presence of voids in shear bands may explain several aspects of mechanical behavior in metallic glasses. For instance, it may explain the fact that metallic glasses show nearly zero plastic strain in uniaxial tension, but can show plastic strains of 1-4% in uniaxial compression. Under tensile loading, the voids would presumably grow and cause fracture, while compressive loading would tend to inhibit void growth and fracture, while allowing plastic deformation to continue. Furthermore, the presence of these voids presumably influences subsequent deformation on the same shear band. This might explain, for instance, the experimental observation that removal and reapplication of a load causes continued deformation on previously existing shear bands.

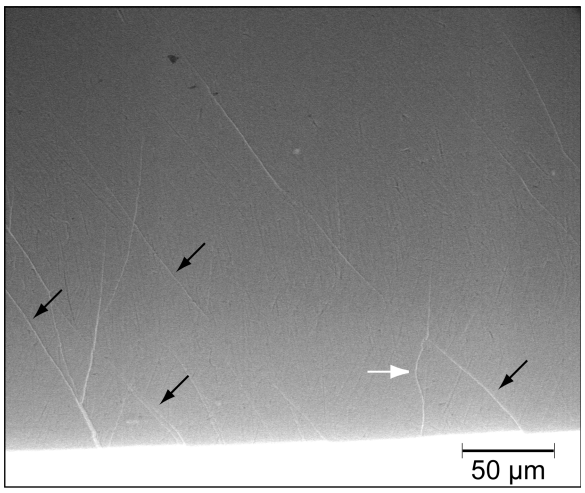

Figure 5: ESEM image of a specimen loading in three-point bending. The loading axis is vertical, so the shear bands (actually slip steps on the surface of the specimen) appear edge-on). The white arrow indicates one of the first shear bands to form, at about the point where the load-deflection curve became nonlinear (Fig. 6). The black arrows indicate "primary" shear bands that are responsible for the majority of plastic deformation.

2.2 Correlation of shear band behavior with constitutive behavior

Many researchers have observed "serrated flow" (abrupt load drops during plastic deformation) in uniaxial compression tests of metallic glasses; with proper instrumentation, serrated flow can even be observed in uniaxial tension. There are two possible explanations for this behavior. One is that each load drop might correspond to the formation of a new shear band. Another possibility is that slip on shear bands might occur intermittently, with each slip event causing a load drop.

To investigate serrated flow, we conducted a series of *in situ* studies of shear band behavior, subjecting metallic glass specimens to three-point bending and uniaxial compression while simultaneously recording load-deflection data and observing the shear band morphology using an environmental scanning electron microscope (ESEM) [12, 13]. Figure 5 shows a typical ESEM image of a bending specimen, with several shear bands apparent. The load-deflection data for this sample are shown in Figure 6, correlated with the shear band density. There is a dramatic multiplication in the number of shear bands from the onset of plastic deformation up to the point of maximum load; beyond the point of maximum load, few new shear bands form, and slip occurs primarily on pre-existing shear bands. The inset to Fig. 6(a) shows a detail of the load-time behavior; the halts and drops in the load are analogous to the load drops observed in uniaxial loading. The halts and drops occur while the number of shear bands is increasing dramatically. In contrast, beyond the point of maximum load, where the shear band density increases slowly (and mostly to the extension of existing bands), we observed no load drops. Thus, we conclude that the load drops are the result of the formation and propagation of new shear bands, rather than intermittent slip on existing shear bands.

We also made measurements of slip offset on shear bands, both *in situ* during deformation,

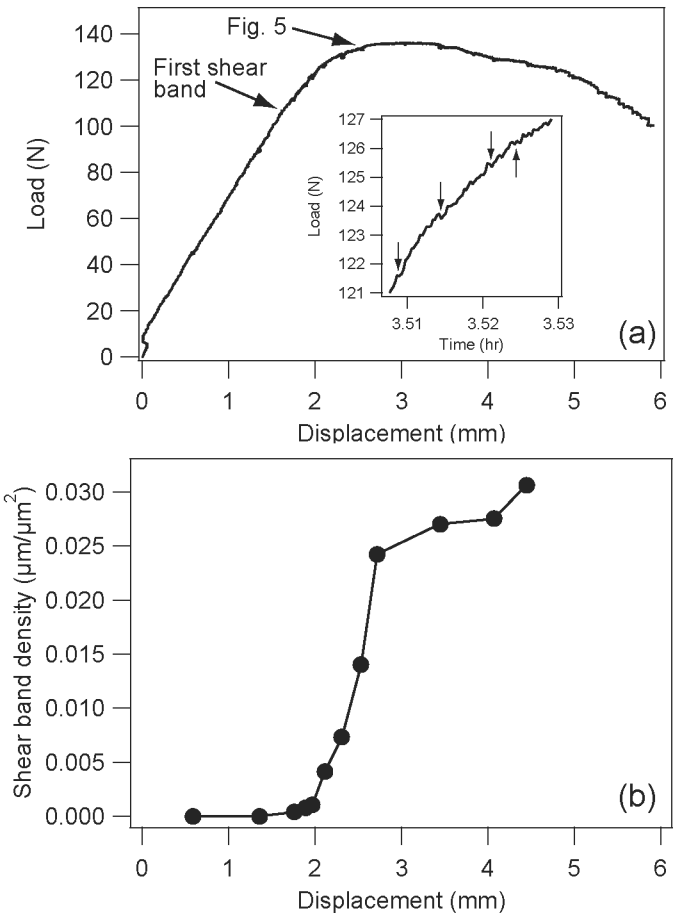

Figure 6: (a) Load-deflection data recorded during three-point bending test. The appearance of the first shear band is indicated, along with the point at which the image in Fig. 5 was taken. (b) Shear band density (total length per unit area) during deformation; notice the dramatic increase in shear band density just after the onset of plastic deformation.

and *ex situ* after testing with the goal of observing features that would indicate the occurrence of discrete slip events on individual shear bands [12,13]. We were able to rule out the existence of very large (> 1 μm) slip events, but the resolution of the *in situ* measurements was not good enough to allow us to observe smaller slip events.

2.3 Publications

Peer-review journals

1. J. Li, Z. L. Wang, and T. C. Hufnagel. "Characterization of nanometer-scale defects in metallic glasses by quantitative high resolution transmission electron microscopy." *Phys. Rev. B*, 65:144201, 2002.

2. J. Li, F. Spaepen, and T. C. Hufnagel. "Nanometre-scale defects in shear bands in a metallic glass." *Phil. Mag. A*, 82:2623, 2002.

3. T. C. Hufnagel, P. El-Deiry, and R. P. Vinci. "Development of shear band structure during deformation of a $Zr_{57}Ti_5Cu_{20}Ni_8Al_{10}$ bulk metallic glass." *Scripta Mat.*, 12:1071, 2000.

Conference proceedings

1. P. A. El-Deiry, R. P. Vinci, N. Barbosa III, and T. C. Hufnagel. "In situ observations of shear band development during deformation of Zr-based bulk metallic glasses." *Mat. Res. Soc. Symp. Proc.*, 644:L 10.2, 2001.

2. J. Li, X. Gu, and T. C. Hufnagel. "Medium-range order in metallic glasses studied by fluctuation microscopy." *Microsc. Microanal.*, 7 Suppl. 2:1260–1261, 2001.

3. J. Li, X. Gu, L.-Q. Xing, K. Livi, and T. C. Hufnagel. "Plasticity at crack tips in Zr-based bulk metallic glasses." *Mat. Res. Soc. Symp. Proc.*, 644:L12.19, 2001.

Papers presented at meetings, but not published

1. T. C. Hufnagel, J. Li, and F. Spaepen. "Structure of shear bands in metallic glasses." Second International Conference on Bulk Metallic Glasses, Keelung, Taiwan, March 25, 2002.

2. T. C. Hufnagel, J. Li, Z. L. Wang, and F. Spaepen. "Nanometer-scale defects in shear bands in metallic glasses." 2002 TMS Annual Meeting, Seattle, Washington, February 19, 2002.

Manuscripts submitted, but not published

None.

Technical reports submitted to ARO

None, aside from Interim Progress Reports and this Final Progress Report.

2.4 Participating scientific personnel

1. Prof. Todd C. Hufnagel (Principal Investigator)
2. Dr. Jing Li (Post-doctoral scholar), now a post-doctoral scholar at Georgia Institute of Technology (with Prof. Z. L. Wang).
3. Xiaofeng Gu (doctoral student), graduation anticipated Februrary, 2003. Has accepted a post-doctoral position at the University of Virginia (with Profs. Gary Shiflet and Joseph Poon).

2.5 Report of inventions

None.

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